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(21) International Application Number: PCT/NL99/00371 (22) International Filing Date: 15 June 1999 (15.06.99) (30) Priority Data: 1009431 18 June 1998 (18.06.98) NL (71) Applicant (for all designated States except US): STICHTING ENERGIEONDERZOEK CENTRUM NEDERLAND [NL/NL]; Postbus 1, NL-1755 ZG Petten (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): VAN ROOSMALEN, Johannes, Adrianus, Maria [NL/NL]; Buizerdweg 16, NL-1826 GG Alkmaar (NL). RIJNBERG, Evelien [NL/NL]; Piraeusplein 28, NL-1019 NN Amsterdam (NL). SOMMELING, Paul, Matthieu [NL/NL]; Marislaan 25, NL-2316 XV Leiden (NL). (74) Agent: DOKTER, Hendrik, Daniël; Octrooibureau Dokter & Mink, P.O. Box 657, NL-7300 AR Apeldoorn (NL).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published With international search report. In English translation (filed in Dutch).	
(54) Title: REVERSED DYE-SENSITIZED PHOTOVOLTAIC CELL			
(57) Abstract Photovoltaic element comprising a layered structure of at least a first electrically conductive layer, a layer of crystalline metal oxide semiconductor material deposited on the first electrically conductive layer, a transparent second electrically conductive layer deposited on a transparent substrate and an electrolytic liquid contained between the layer of semiconductor material and the second electrically conductive layer, wherein the layer of semiconductor material is deposited on a metal foil, which metal foil forms the first electrically conductive layer.			

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REVERSED DYE-SENSITIZED PHOTOVOLTAIC CELL

The invention relates to a photovoltaic element comprising a layered structure of at least a first electrically conductive layer, a layer of crystalline metal oxide semiconductor material deposited on the first electrically conductive layer, a transparent second electrically conductive layer deposited on a transparent substrate and an electrolytic liquid contained between the layer of semiconductor material and the second electrically conductive layer.

10 Such an element is known from the American patent no. 5,350,644.

 The known photovoltaic cell comprises a light-transmitting electrically conductive layer which is deposited on a glass plate or a transparent polymer foil to which a number of preferably porous layers of titanium dioxide have been applied and wherein at least the last titanium dioxide layer is doped with a divalent or trivalent metal ion. The combination of titanium dioxide and conductive layer forms the photoelectrode of a solar cell, which solar cell further comprises a light-transmitting second electrically conductive layer which is deposited on a light-transmitting substrate and which forms a counter-electrode. Received between photoelectrode and counter-electrode is an electrolyte acting as redox system. The operation of the known solar cell is as follows. A photon from the visible light incident via the counter-electrode releases an electron at the interface of titanium dioxide and electrolyte from an electron-hole combination, which electron disappears in the conduction band of the titanium dioxide and is discharged via the electrically conductive layer of the photoelectrode. The resulting hole is supplemented with an electron from the electrolyte, while the electrolyte accepts an electron from the counter-electrode. The acceptance of electrons by the electrolyte can be enhanced by a catalyst applied to the surface of the

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counter-electrode, while the efficiency of the solar cell can be increased by a sensitizer dye on the surface of the titanium dioxide layer, which dye absorbs light and herein acquires an energy-rich state and is able to inject an
5 electron with an efficiency of almost 100% into the conduction band of the titanium dioxide.

Such a known solar cell has a number of disadvantageous properties which stand in the way of large-scale application of this cell. Inherent in the use of glass as transparent
10 substrate material is a determined thickness of a solar cell which makes the cell unsuitable for use for instance in particular products in the field of consumer electronics, such as watches. It is known that replacing glass with a transparent plastic results in a loss of efficiency of the
15 solar cell.

It is an object of the invention to provide a solar cell of very small thickness which has a high efficiency when transparent polymer foil is used as substrate material and which can be assembled in large quantities in simple
20 manner.

This objective is achieved and other advantages gained with a photovoltaic element of the type stated in the preamble, wherein according to the invention the layer of semiconductor material is deposited on a metal foil, which
25 metal foil forms the first electrically conductive layer.

In the solar cell according to the invention light impinges upon the semiconductor material via the transparent counter-electrode and the electrolytic liquid between the counter-electrode and the semiconductor material. The most
30 obvious manner of light incidence in the known cell, i.e. via the photoelectrode, is precluded by use of the non-transparent metal foil. A photovoltaic element according to the invention is a "reversed solar cell".

Surprisingly, it has now been found that the efficiency
35 of a reversed solar cell according to the invention is higher than in a known, above described solar cell, wherein the photoelectrode is impinged upon directly, and not via the electrolytic liquid, by the photons of incident

sunlight. The cause of the recorded increase in efficiency is sought in the fact that application of a metal foil as substrate material enables sintering of the layer of semiconductor material at higher temperatures than in a known solar cell with a substrate of polymer material.

In an advantageous embodiment the metal foil is substantially a zinc foil.

In another advantageous embodiment the metal foil is substantially a titanium foil.

With the use of a zinc or titanium foil a skin of zinc oxide respectively titanium oxide results when the semiconductor layer deposited thereon is sintered, which skin on the one hand forms a protection for the underlying zinc respectively titanium foil and on the other forms a good electrical conductor owing to its photoelectric properties.

The semiconductor material in a photovoltaic element according to the invention is for instance zinc oxide, tin oxide or, preferably, titanium dioxide.

The layer of semiconductor material preferably comprises a layer of photo-sensitization material deposited thereon, in particular a photo-sensitive dye, which is selected from suitable dyes known per se in the field.

The transparent substrate in a photovoltaic element according to the invention may comprise glass and in an advantageous embodiment comprises a foil of flexible plastic material, preferably polyethylene terephthalate (PET).

The invention will now be elucidated hereinbelow on the basis of embodiments and with reference to the drawings.

In the drawings

Fig. 1 shows in schematic cross-section a first embodiment of a solar cell according to the invention, and

Fig. 2 shows in schematic cross-section a second embodiment of a solar cell according to the invention.

Corresponding components are designated in the figures with the same reference numerals.

Fig. 1 shows the layered structure of a solar cell 22, which is substantially built up of a titanium foil 23, a

porous layer of nanocrystalline titanium dioxide 14, a layer 15 of a suitable dye-sensitizer, a lithium iodide/iodine solution 16 and a glass substrate 21 on which a layer 18 of a transparent conductive oxide (TCO) is deposited. Layer 15 is shown in greatly simplified manner. In reality the dye-sensitizer is applied in a solution to semiconductor layer 14 and penetrates into the pores thereof, so that the dye covers the whole semiconductor surface. The layer of titanium dioxide 14 is formed in accordance with a per se known method by sintering a dispersion of colloidal particles of titanium dioxide onto titanium foil 23, wherein between the sintered titanium dioxide 14 and titanium foil 23 a layer of titanium dioxide 28 results which protects the underlying layer 23 against the corrosive action of the lithium iodide 16. The figure further shows a layer 19 (not shown to scale) of a catalyst, for instance carbon, for the conversion of neutral I in the lithium iodide solution to I^- by accepting an electron from counter-electrode 18. In this solar cell 22 light (indicated by arrows designated $h\nu$, wherein h represents Planck's constant and ν the frequency of the incident light) is incident on dye layer 15 via counter-electrode assembly 21, 18, 19 and the lithium iodide solution 16.

Fig. 2 shows an embodiment of a solar cell 25 as alternative to the solar cell shown in Fig. 1, wherein counter-electrode 18 is deposited on a flexible foil 26 of PET, whereby a flexible and very thin solar cell is obtained.

It is noted that the examples given here serve to elucidate the invention, not to limit the scope thereof. A "reversed" dye-sensitized solar cell according to the invention can for instance also contain, instead of the above mentioned lithium iodide, another per se known suitable electrolyte such as potassium bromide or potassium iodide.

CLAIMS

1. Photovoltaic element comprising a layered structure (22, 25) of at least
a first electrically conductive layer (23),
a layer of crystalline metal oxide semiconductor
5 material (14) deposited on the first electrically conductive layer (23),
a transparent second electrically conductive layer (18) deposited on a transparent substrate (21, 26), and
an electrolytic liquid (16) contained between the layer
10 of semiconductor material (14) and the second electrically conductive layer (18), characterized in that the layer of semiconductor material (14) is deposited on a metal foil (23), which metal foil forms the first electrically conductive layer (23).
- 15 2. Photovoltaic element as claimed in claim 1, characterized in that the metal foil (23) is substantially a zinc foil.
3. Photovoltaic element as claimed in claim 1, characterized in that the metal foil (23) is substantially a
20 titanium foil.
4. Photovoltaic element as claimed in any of the claims 1-3, characterized in that the semiconductor material (14) is zinc oxide or tin oxide.
5. Photovoltaic element as claimed in any of the claims
25 1-3, characterized in that the semiconductor material (14) is titanium dioxide.
6. Photovoltaic element as claimed in any of the foregoing claims, characterized in that the layer of semiconductor material (14) comprises a layer of photo-
30 sensitization material (15) deposited thereon, in particular a photo-sensitive dye.
7. Photovoltaic element as claimed in any of the foregoing claims, characterized in that the transparent

substrate comprises a foil of flexible plastic material
(26).

8. Photovoltaic element as claimed in claim 7,
characterized in that the plastic material is polyethylene
5 terephthalate (PET) (26).

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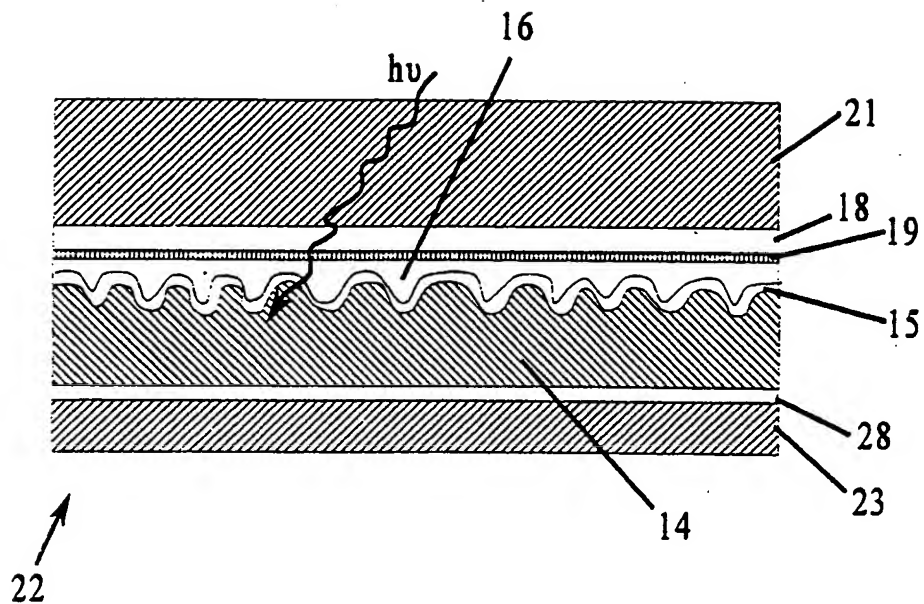


Fig. 1

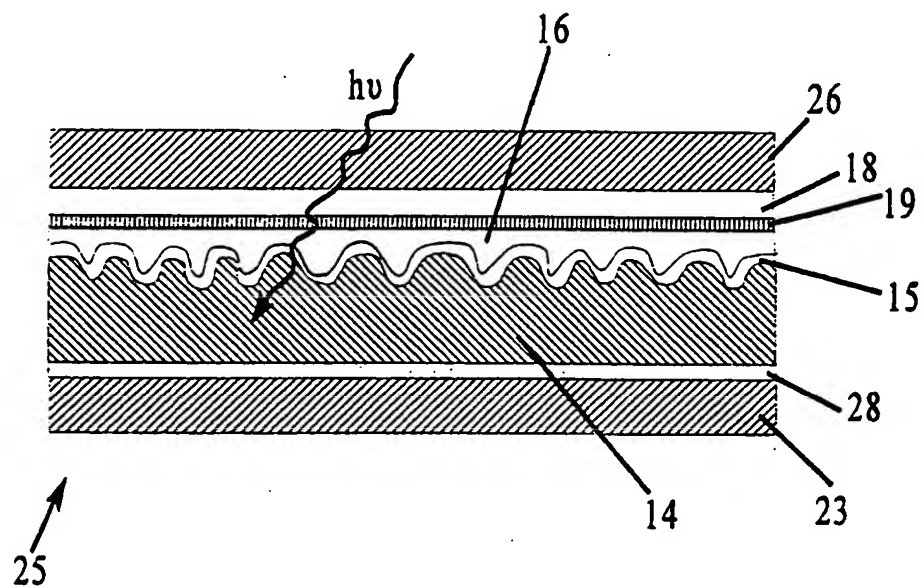


Fig. 2

INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 99/00371

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 H01G9/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 927 721 A (GRATZEL MICHAEL ET AL) 22 May 1990 (1990-05-22) column 3, line 21 - line 39 column 4, line 7 - line 18; figure 1 ---	1,3-5
X	US 5 350 644 A (GRAETZEL MICHAEL ET AL) 27 September 1994 (1994-09-27) cited in the application column 15, line 8 - line 28; figure 1 ---	1,3,5,6
A	WO 97 15959 A (SONCEBOZ EBAUCHES FAB ;HAMPEL REINHARD GEORG OTTO (FR); MEYER ANDR) 1 May 1997 (1997-05-01) page 4, line 27 - line 36 --- -/--	1,7,8

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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information on patent family members

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